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Effect of the Salts of the Lyotropic Series on the

Farinograph Characteristics of Milk-Flour Dough

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SKOVHOLT AND BAILEY (1) first reported that salt effects may offer means of controlling the baking properties of nonfat dry milk (NFDM). The addition of calcium salts to whey (2) has been reported to enhance the baking quality of whey with flour. It has also been noted that the addition of sodium chloride decreased the farinograph consistency of doughs (3,4). However, Moore and Herman (5) reported that the addition of 3 and 4% sodium chloride increased consistency. They also reported that 4 to 8% NFDM sequentially increased absorption, arrival times, and stability values. The full absorptive effects of flour plus 6% NFDM was not realized unless sodium chloride was added to doughs (1).

Hofmeister (6) was among the first workers to report that valency is not the only factor involved in the behavior of ions toward a colloid system, and that monovalent ions possessed within themselves varying ability to precipitate sols. Accordingly, he arranged them in an order referred to as the lyotropic series. In the anion series, citrate showed the most precipitating effect, followed by tartrate, sulfate, acetate, chloride, nitrate, bromide, and thiocyanate. The cation effects are less marked; they followed in the order of barium, strontium, calcium, potassium, sodium, and lithium, the last showing the least precipitating effect. Fruendlich (6) suggested that the series correspond to the order of the hydration of ions.

This paper reports the effect of the addition of ions of the lyotropic series on the mix properties of flour and flour-NFDM doughs as measured by the farinograph. The anions are added as their sodium salts, the cations as chlorides. Also presented is the effect of NaCl on the farinograph characteristics of flour doughs containing either NFDM, supercentrifuged casein, or whey.

Materials and Methods

Flours. Two commercial flours were used: a hard red winter wheat (HRWW) flour that was malted and bleached, containing 11.5% protein and 0.44% ash, and a hard red spring wheat (HRSW) flour that was bromated, bleached, and malted, containing 12.7% protein and 0.40% ash.

Nonfat Dry Milk. High-heat NFDM was prepared by forewarming fresh skim milk to 88°C. for 30 min., concentrating to 41% total solids in a Wiegand falling film evaporator at 50°C. under vacuum, and spray-drying in a Grey-Jensen conical dryer. The dry milk contained 4.4% moisture and 1.0 mg. whey protein N per g. solids. For fractionation purposes, the dry milk was adjusted to a 9.18% total solids level.

Milk Fractions. Casein and whey were prepared from unheated and high-heat-treated (88°C. for 30 min.) skim milks by supercentrifugation of the samples for 90 min. at 44,000 × *g*. The resulting whey supernatant (containing about 9% of the total casein which was noncentrifuged) and the casein pellet (containing 3.4% of its total protein from the admixed whey) were then freeze-dried. The casein and whey were then added to flour in the same ratio they occur in a 6% NFDM level.

Casein protein was determined by a Kjeldahl N assay in unheated milk fractions as the material precipitated at pH 4.6. Whey protein is the protein soluble at pH 4.6.

Farinograph. A model PL 2H farinograph equipped with a 300-g. bowl held at 30°C. was used. The mixer rotated at 63 r.p.m. Water content of the doughs was varied to center the curves on the 500-B.U. line. Absorptions were all corrected to a 480-g. dough weight by the method of Stamberg and Merritt (7), in which it was calculated that 20 g. dough weight adds 20 B.U. equivalent to 0.7% water absorption. The conversion was checked with a 540-g. and a 480-g. dough mass and found to be valid with little or no change in other farinograph characteristics. Analytical reagent-grade salts and NFDM were added to the flour and preblended in the farinograph bowl before titration in the water. Where necessary, corrections for the water contained in some of the salts as water of hydration were made in the absorption values reported. All absorptions were calculated on a 14% flour moisture basis.

pH. The pH of doughs was taken by immersing the electrodes of the Beckman Zeromatic pH meter directly in the doughs after mixing.

Effect of Anions of Sodium Salts

Absorption. Figure 1 shows the effect of 0.1 equivalent concentrations of the sodium anions on the farinograph absorption of HRWW flour and flour-6% NFDM doughs. These cations, arranged in an order

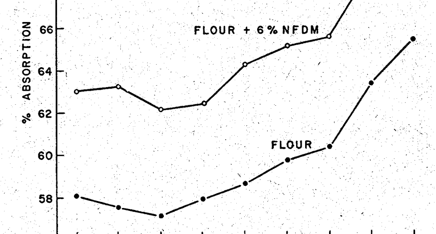

Fig. 1. Effect of anions of sodium salts on absorption of doughs.

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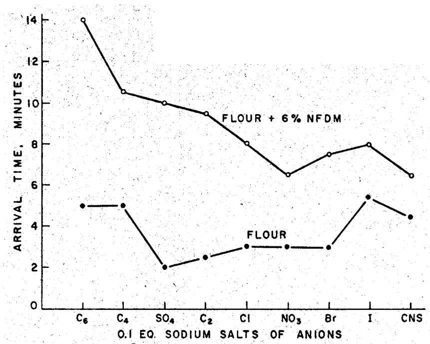

Fig. 2. Effect of anions of sodium salts on arrival times of doughs.

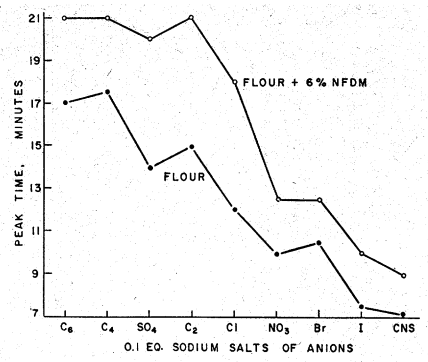

Fig. 3. Effect of anions of sodium salts on peak times of doughs.

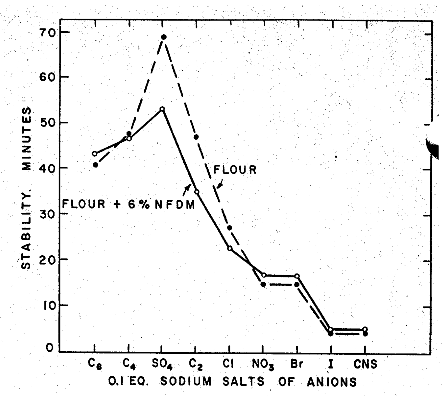

Fig. 4. Effect of anions of sodium salts on stability values of doughs.

of increasing lyotropic action, are: citrate (C_6), tartrate (C_4), SO_4, acetate (C_2), chloride, nitrate, bromide, iodide, and thiocyanate. A 0.1 equivalent concentration is equal to 1.95% sodium chloride, basis of flour. Absorption increases occur in both flour and flour-NFDM doughs as the series is ascended from the citrate to the thiocyanate end. This order of absorption increase is inversely related to the hydration of anions; the most hydrated is the citrate anion and least hydrated is the thiocyanate anion. This order may also be stated as directly related to the lyotropic action of these anions. A relatively constant difference of 5 to 6% absorption is noted between flour-6% NFDM doughs and flour doughs.

Arrival Times. Figure 2 shows the effect of these anion salts on the arrival time (in min.) of flour and flour-NFDM doughs. With flour the shortest arrival times are associated with the sulfate, acetate, chloride, nitrate, and bromide salts. On the other hand, in flour-NFDM doughs, nitrate, chloride, and bromide salts give the shortest arrival times, and organic acid salts and sulfate give the longest. Flour-NFDM doughs produce longer arrival times than flour doughs.

Peak Times. Figure 3 shows the effect of the anion salts on the peak times of both doughs. It shows that flour-NFDM produces higher peak-time values than flour doughs. Highest peak-time values are obtained with both doughs in the presence of anions of organic acids and lowest with the least hydrated thiocyanate ions.

Stability Values. Figure 4 shows the effect of sodium anions on farinograph stability values. With both NFDM and NFDM-free doughs, sodium salts of the organic acids and sulfate give higher stability values than sodium chloride. On the other hand, nitrate, bromide, and especially iodide and thiocyanate anions give lower values. Flour doughs with chloride, acetate, and sulfate salts produce higher stability values than flour-NFDM doughs.

Effect of Cations of the Chloride Salts

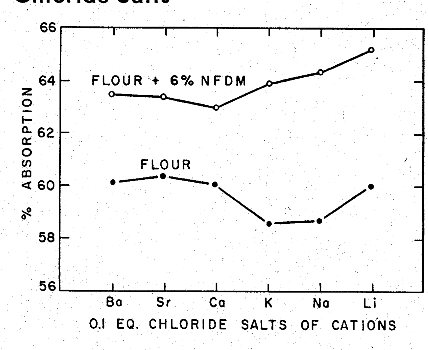

Fig. 5. Effect of cations of chloride salts on absorption of doughs.

Absorption. Figure 5 shows the effect of chloride cations on the absorption of HRWW flour and flour-NFDM doughs. Chloride cations, added at a 0.1 equivalent concentration and arranged in an order of increasing lyotropic action, are: barium, strontium, calcium, potassium, sodium, and lithium. These salts all produce much the same absorption within each type of dough. Absorption differences between flour and flour-NFDM doughs of the divalent salts are about 3%; those of the monovalent salts are about 5.5%.

Arrival Times. Figure 6 shows the effect of the cationic salts on the arrival times of flour-NFDM and flour doughs. Monovalent salts increase arrival times of flour-NFDM doughs much more than divalent cationic salts. On the other hand, these salts do not influence the arrival times of flour doughs to any great extent. Flour-NFDM doughs produce longer arrival times than flour doughs.

Peak Times. Figure 7 shows the effect of the cation salts on peak times. It shows that flour-NFDM doughs produce higher peak-time values than flour doughs. Higher peak-time values are associated with monovalent cation salts than with the divalent cation salts.

Stability Values. Figure 8 shows the effect of the cation salts on the stability (minutes) of flour doughs and flour-NFDM doughs. The monovalent salts produce higher

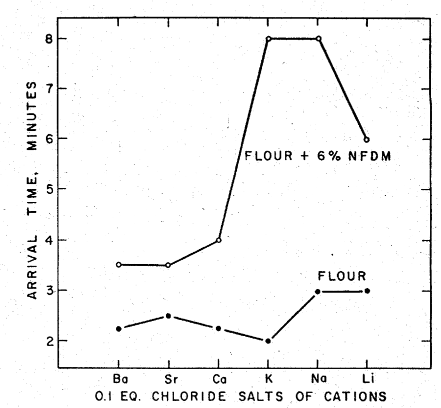

Fig. 6. Effect of cations of chloride salts on arrival times of doughs.

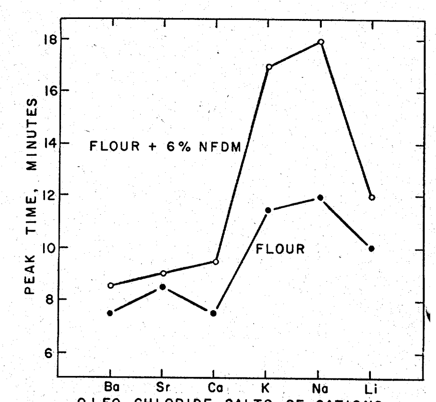

Fig. 7. Effect of cations of chloride salts on peak times of doughs.

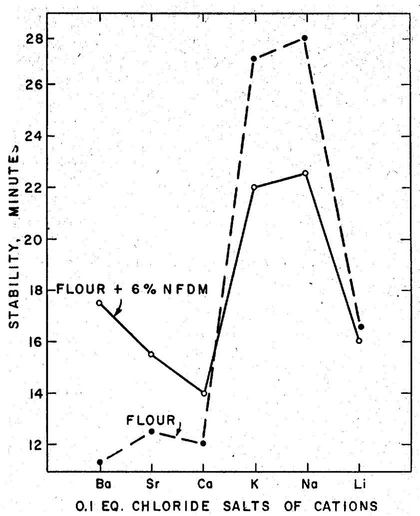

Fig. 8. Effect of cations of chloride salts on stability values of doughs.

stability values than the divalent salts in flour doughs. In the divalent salt series, flour-NFDM doughs produce higher stability values than flour doughs. With the monovalent salts, the opposite is observed.

Effect of Sodium Chloride on NFDM, Supercentrifuged Casein, and Whey

Table I shows the influence of sodium chloride and 6% NFDM on farinograph patterns of HRSW flour. Sodium chloride decreases the absorption of flour doughs. Addition of skim milk increases absorption, and addition of salt increases the absorption of flour-NFDM doughs still more. There is a 5.7% absorption difference between a salt-flour dough and a salt-NFDM dough, indicating that adding 6% NFDM increases the water-binding capacity by a like amount. Sodium chloride increases stability values of the flour as well as those of the flour-NFDM doughs. Salt increases the arrival times of flour-NFDM doughs but not, to any extent, that of the flour doughs. Similar differences in absorption and mix patterns, not shown, were obtained with HRWW flour as well as with complete doughs containing 5% sugar, 3% shortening, 2% yeast, and 0.5% malt.

Table I. Influence of NaCl and NFDM on the Farinograph Characteristics of HRSW Flour

NFDM, 6%	*NaCl, 2%*	*Absorption*	*Arrival Time*	*Stability*
		%	*min.*	*min.*
+	+	63.4	8.0	32.0
+	—	61.4	2.5	26.5
—	—	60.0	2.5	18.5
—	+	57.7	3.0	41.0

Table II shows the effect of high-heat NFDM, supercentrifuged casein, and whey from the milk, all in the presence of salt, on farinograph characteristics. Absorption values are also shown for these fractions in the absence of salt. The further increase in absorption of NFDM containing doughs noted on addition of NaCl was related to changes in the casein fraction. The addition of whey to flour doughs did not affect absorption. Relative to NFDM doughs, NaCl added to whey decreases arrival times and increases stability values. The absolute stability value of the whey dough was close to that of the flour in the presence of salt.

Table II. Influence of High-Heat-Treated NFDM and Its Milk Fractions on Farinograph Characteristics of HRSW Flour

	Absorption		*Arrival Time*	*Stability*
	%	*%*	*min.*	*min.*
Salt, 2%	—	+	+	+
NFDM, 6%	61.4	63.4	8	32
Casein, 1.8%	62.0	62.9	7	35
Whey, 4.2%	59.6	58.4	6	38
Flour	60.0	57.7	3	41

Table III is similar to Table II except that the effects of unheated NFDM and its fractions are tabulated. The results here are similar to those found in Table II, with the exception that stability values of the unheated milk doughs are much lower and the arrival time of the dough containing NFDM is slightly larger.

Discussion

Bayfield and Young (8) report that pH affects farinograph characteristics of complete doughs without shortening. Decreases of pH from 6.2 to 5.4 decrease consistency from 540 to 455 B.U.—equivalent to about 3.5% absorption—and increase peak time from 14 to 17 min.

Table IV shows the effect of the lyotropic salts on dough pH values. Although the pH values of Na anion doughs are relatively constant in the series from Cl to CNS, absorption

Table III. Influence of Unheated NFDM and Its Milk Fractions on the Farinograph Characteristics of HRSW Flour

	Absorption		*Arrival Time*	*Stability*
	%	*%*	*min.*	*min.*
Salt, 2%	—	+	+	+
NFDM, 6%	62.5	63.4	9.5	9
Casein, 1.8%	62.0	63.4	7.5	12
Whey, 4.2%	59.6	57.6	5.5	24

sequentially increased about 6%. It was also observed that pH differences between doughs containing Na_2SO_4 and either Na acetate or Na tartrate had little effect on absorption characteristics. The effect of pH on peak-time values was considered to be negligible. In the cation salt series, absorption differences observed are smaller; in the case of the flour doughs, those doughs containing monovalent cations with higher pH values actually produced slightly lower absorptions than those of the divalent cations of lower pH. Over-all effects of pH on absorption and peak-time values were considered to be negligible with either flour or flour-NFDM doughs.

Even though the farinograph is one of the most widely used instruments in cereal laboratories and numerous papers have been published dealing with its application to problems concerning dough mixing and baking, the interpretation of data obtained by its use remains difficult.

When the farinograph is operating near the peak of the mixing curve, the torque applied to maintain constant mixing speed may be considered to be related to the viscosity of the system being mixed. Since this recorded torque is a function of the water content of the mixture, a crude concentration *vs.* viscosity plot can be visualized from farinograph data, and factors influencing this relationship can be studied.

In classic rheology, viscosity increases in colloid systems, of constant solids content, must arise from

Table IV. Effect of Lyotropic Salts on pH of Doughs

Added anions	$C_6H_5O_7^{=}$	$C_4H_4O_6^{=}$	$SO_4^{=}$	$C_2H_3O_2^{-}$	Cl^{-}	NO_3^{-}	Br^{-}	I^{-}	CNS^{-}
pH, flour	6.50	5.85	5.90	6.40	5.85	5.91	5.82	5.92	6.00
pH, flour-NFDM	6.62	6.10	5.98	6.40	6.10	6.02	6.00	6.10	6.10
Added cations	Ba^{++}	Sr^{++}	Ca^{++}	K^{+}	Na^{+}	Li^{+}			
pH, flour	5.60	5.60	5.50	5.90	5.85	5.80			
pH, flour-NFDM	5.56	5.62	5.51	6.12	6.10	6.00			

an increase in hydration of the suspended material, an increase in asymmetry of the particles present, or particle size growth by interaction. During dough mixing, it is highly probable that all three mechanisms are operative. Some insight into the manner in which added salts affect these actions in bread doughs can be gained from a study of the effect of adding salts of the lyotropic series.

Since it was observed that absorption of water by doughs was more greatly influenced by the nature of the added anion than by the lyotropic properties of the added cation, it is probable that sites having a positive charge are primarily responsible for maintaining structure conducive to water-binding. The binding of cations by dough, even though it is thought to be minor (9), certainly occurs, as demonstrated by their influence on the peak times and stabilities of the mixtures. However, these effects seem to be more influenced by the valence of the cation than its position in the lyotropic series.

The mechanical mixing in the farinograph is thought to promote molecular distortion and interactions leading to the formation of a three-dimensional structure of gel type. The water-holding capacity and swelling of gels in general are sometimes pictured as resulting from the disruption or loosening of junction points within the gel network. Hermans (10) has postulated that the chance of junction disruption increases with the increase in lyotropic properties of an ion, when the partial free energy of the junction point separation promoted by the addition of bound water accompanying an ion is less than the partial free energy change caused by the rise in salt concentration due to water release.

It can also be considered that the binding of certain anions in doughs actually promotes the formation of weak hydrophobic bonds between macromolecules by partial dehydration of their surfaces. This process would be promoted by the binding of the least-hydrated ions or those highest in the lyotropic series. These bonds would be essentially weak but of sufficient strength to immobilize enough ions to allow osmotic forces to move water into the dough mass. However, these bonds could easily be disrupted by shear, and it is possible that the low peak times and dough stabilities observed in dough containing anions high in the lyotropic series reflect the development of dough structure primarily through the formation of lyophobic bonds.

Regardless of the structure of the bonds produced during the first stage of mixing, the addition of highly lyotropic anions tends to set conditions leading to the rapid breakdown of the dough under continued stress.

In doughs containing NFDM the picture is complicated by the fact that the anions, on the low end of the lyotropic scale, chelate calcium or form insoluble salts in its presence. These anions should disrupt or loosen the casein micelle and convert it into random chains of sodium caseinate.

Evidence for the development of dough structure, in some instances, by hydrophobic intermolecular bonding can again be seen when salts of the lyotropic series are added to doughs containing casein. Here increase in adsorption follows the increase in lyotropic action of the added anions. The casein molecule is thought to be partially lyophobic and could bond to the flour protein through weak tertiary bond When the doughs were made up with the more completely solvated whey proteins, no similar effects were observed. In fact, addition of whey to doughs led to a decrease in their water-absorption.

A consideration of the action of lyotropic anions in determining the mixing properties of doughs, as measured by the use of the farinograph, leads to the conclusion that some doughs develop by formation of weak tertiary intermolecular bonds of lyophobic nature; while the formation of those bonds can lead to increased water-absorption, they do not create a strong dough. No similar relation between the lyotropic properties of added cations and mixing characteristics of doughs could be found.

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